

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
21 December 2000 (21.12.2000)

PCT

(10) International Publication Number  
WO 00/76637 A1

(51) International Patent Classification<sup>7</sup>: B01D 53/94,  
53/86 MN Nijmegen (NL). VAN YPEREN, Renee [NL/NL];  
Zonnedaauw 7, NL-6961 PL Eerbeek (NL).

(21) International Application Number: PCT/NL00/00404 (74) Agent: PRINS, A., W.; Vereenigde, Nieuwe Parklaan 97,  
NL-2587 BN The Hague (NL).

(22) International Filing Date: 13 June 2000 (13.06.2000)

(81) Designated States (national): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE,  
DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU,  
ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS,  
LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO,  
NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR,  
TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(25) Filing Language: Dutch  
(26) Publication Language: English  
(30) Priority Data:  
1012296 11 June 1999 (11.06.1999) NL

(84) Designated States (regional): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian  
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European  
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,  
IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG,  
CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant (for all designated States except US): GASTEC  
N.V. [NL/NL]; Wilmersdorf 50, NL-7327 AC Apeldoorn  
(NL).

Published:

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(72) Inventors; and

(75) Inventors/Applicants (for US only): JELLES, Sytse,  
Jelle [NL/NL]; Kazernestraat 51, NL-2514 CS Den  
Haag (NL). BOUWMAN, Willem, Hendrik [NL/NL];  
Sluiswachtershoeve 201, NL-7326 ZC Apeldoorn (NL).  
VAN NISSELROOIJ, Petrus, Franciscus, Maria,  
Theresia [NL/NL]; Van Welderenstraat 50, NL-6511

WO 00/76637 A1

(54) Title: METHOD FOR REMOVING NITROGEN OXIDES FROM AN OXYGEN-CONTAINING GAS STREAM

(57) Abstract: A process for removing nitrogen oxides from a gas stream containing nitrogen oxides and oxygen involves bringing the gas stream into contact with a reducing gas stream in the presence of a deNO<sub>x</sub> catalyst. The reducing gas stream contains CO, H<sub>2</sub> and, optionally, NH<sub>3</sub>; it is produced by reacting hydrocarbons with the oxygen from the above mentioned nitrogen oxide- and oxygen-containing gas stream. A catalyst, such as an oxidising or stream-reforming catalyst may be used to promote the reaction which produces the reducing gas stream.

**Title: Method for removing nitrogen oxides from an oxygen-containing gas stream**

This invention relates to a catalytic conversion of nitrogen oxides to molecular nitrogen, which nitrogen oxides are formed upon combustion of hydrocarbons and/or synthesis gas (H<sub>2</sub>/CO). More particularly, it relates to the conversion of nitrogen oxides in the presence of oxygen such as these are formed, for instance, in the operation of units such as combustion engines under so-called poor or 'lean-burn' conditions, that is: under combustion conditions where an excess of oxygen is present. The invention further relates to the conversion of nitrogen oxides which may be formed in industrial processes, such as nitric acid production.

In the combustion of hydrocarbons with molecular oxygen (for instance originating from air), oxides of nitrogen may be formed due to the prevailing temperature and pressure during the combustion process. These nitrogen oxides, among which NO and NO<sub>2</sub> (usually denoted by NO<sub>x</sub>) are very harmful to the environment. Nitrogen oxides are held responsible inter alia for the formation of acid rain and photochemical smog.

Different methods for reducing NO<sub>x</sub> emission are known and a number of them are already being applied in practice.

Reducing NO<sub>x</sub> emission in stoichiometrically running engines is often accomplished by making use of a so-called three-way catalyst system. The NO<sub>x</sub> conversion catalyst in such systems is capable of converting nitrogen oxides to harmless compounds by reacting them with the reducing combustion products present in the exhaust gas, such as hydrocarbons and CO, to form N<sub>2</sub>.

Generally, the known three-way catalysts which effect the reduction of nitrogen oxides are incapable of performing this conversion in the presence of a considerable amount of oxygen.

This is a problem in particular in the removal of nitrogen oxides from the exhaust gases of the above-mentioned lean-burn engines, such as lean-burn gas turbines, diesel engines, gas engines and off-gases of industrial processes, since in such gases, in addition to nitrogen oxides, a considerable amount of oxygen is present. Moreover, hydrocarbons and/or

CO are not present, or present in an insufficient amount, which is a bar to the successful operation of the above-mentioned three-way catalyst systems.

In installations where a considerable amount of oxygen is present in the exhaust gas, therefore, often an amount of reductant is added. The 5 nitrogen oxides can then be converted by the reductant in the presence of a suitable catalyst (deNO<sub>x</sub> catalyst). This method is known as the so-called Selective Catalytic Reduction (SCR).

Widely used reductants for the SCR reaction are ammonia and urea. Also, it is known from the literature to use hydrocarbons such as 10 ethylene, propylene and propane as reductant (see, for instance, G.P. Ansell *et al.*, 'Mechanism of the lean NO<sub>x</sub> reaction over Cu/ZSM-5', *Appl. Catal. B*, 2 (1993), pp. 81-100). Other possible reductants are, for instance, CO, H<sub>2</sub> and CH<sub>4</sub>, ethanol, hydrocarbons, in particular fuels such as gasoline and diesel oil.

Used most by far as reductant in practical SCR applications, however, are ammonia or urea, or an aqueous urea solution. The use of these agents entails a number of disadvantages. Dosage is extremely critical. If too large an amount of ammonia or urea is charged to the deNO<sub>x</sub> catalyst (i.e., more than is necessary to convert the nitrogen oxides), this 20 will lead to so-called ammonia slip. The emission of ammonia from such installations is actually even more harmful from an environmental point of view than the emission of NO<sub>x</sub>. Also, it is possible that through oxidation of ammonia, this excess dosage leads to the production of NO<sub>x</sub>, which is the very opposite of the object contemplated, viz. reducing the NO<sub>x</sub> emission.

Another disadvantage of the use of ammonia or urea is the necessary 25 storage thereof and the necessity of periodically supplementing the supply if this is not produced within battery limits. In particular ammonia is very dangerous and noxious and the transport thereof involves great safety and environmental risks. As a consequence of all this, both the investment costs and the operational costs of this technique are high.

Although the choice of other reducing agents, such as, for instance, the above-mentioned hydrocarbons, might partly solve these problems, there still remain disadvantages, such as the necessity of separate transport and storage. The attendant safety and environmental hazards are often 35 unacceptable.

This problem would be solved by using as a reducing agent the same fuel that is used or is present in the engine, the (gas) turbine or the combustion process in industrial processes. The hydrocarbons which are present in, for instance, diesel oil and gasoline, however, prove not to be 5 sufficiently active to convert NO<sub>x</sub> under process conditions with an acceptable rate and selectivity.

It is known to start from an SCR catalyst, with the required reducing agent being manufactured from an available source of hydrocarbons, such as methanol, LPG and natural gas, optionally under 10 addition of H<sub>2</sub> which has been obtained from electrolysis or which is stored in storage tanks.

In DE-A-44 04 617 a technique is described whereby, using an electrically heated reactor, a hydrocarbon-containing fuel is catalytically cracked at 200 to 700°C and the cracking products are further activated 15 with air before they are added as reducing agent to the exhaust gas, whereupon the total gas stream is passed over an SCR catalyst.

According to DE-A-196 00 558, also cracked hydrocarbons are used as reducing agent. These hydrocarbons have been obtained from diesel. According to this known method, under SCR conditions, hydrogen is added 20 to the exhaust gas to reduce NO<sub>x</sub> over the SCR catalyst where the cracked hydrocarbons are not sufficiently active. The hydrogen originates from a storage tank or is made through electrolysis or methanol reforming.

The addition of hydrogen as reducing agent for the reduction of NO<sub>x</sub> in the exhaust gases of continuous combustion processes is described 25 in DE-A-42 30 408. There, too, the hydrogen can be obtained by electrolysis or from reforming through steam reforming or partial oxidation (PO) of hydrocarbon containing fuel. To obtain a hydrogen stream with as little carbon monoxide as possible, two shift reactors are placed behind the reformer to convert the CO for the most part with water vapor to form 30 hydrogen and CO<sub>2</sub>.

The use of in situ produced hydrogen as a reducing agent for the reduction of NO<sub>x</sub> from exhaust gas of internal combustion engines is described in EP-A-0 537 968. In this document, the technique of reforming (steam reforming and partial oxidation) of hydrocarbon containing fuels is 35 described. According to this publication, the conditions must be chosen such

that the amount of CO in the hydrogen is so low that the CO concentration cannot yield any problems regarding emissions. The temperature needed for reforming is achieved by making use of the heat of the exhaust gases. The reduction of NO<sub>x</sub> is carried out over an SCR catalyst. As oxidizing agent for 5 the partial oxidation, air is mentioned.

According to the present invention, in a reductant-forming step, hydrocarbons are converted to a reductant stream under suitable conditions, optionally by contacting them with a reductant forming catalyst. The hydrocarbons in the product stream of the reductant forming step can 10 be unreacted hydrocarbons from the feedstock of this step, but may also be smaller hydrocarbons which have been formed by cracking reactions during the reductant forming step.

The reductants can be prepared, by the use of a reductant forming catalyst, from, for instance, residues of hydrocarbons which are contained in 15 the exhaust gas of the unit in which the combustion takes place. It is also possible to draw these hydrocarbons from a different source, for instance the fuel for the combustion unit, which is already available in situ. Combinations of effluent and such a different source are naturally also 20 possible. The oxygen needed for this step at least partly originates from the off-gas to be treated, i.e., the nitrogen oxide- and oxygen-containing gas. Preferably, substantially all oxygen present in the part of the off-gas used for the reductant formation is used for forming the reducing gas stream. The hydrocarbons present in this portion of the off-gas can also be converted 25 to reducing compounds in this step. The hydrocarbons present in the off-gas can then also be converted to reducing compounds in this step.

Through the use of a suitable reductant forming process, optionally utilizing a catalyst, the reductants necessary for the catalytic reduction of NO<sub>x</sub>, in the form of CO and/or H<sub>2</sub>, optionally supplemented with hydrocarbons, can be prepared from hydrocarbons in situ, so that the 30 above-outlined drawbacks in removing NO<sub>x</sub> under oxygen-rich conditions can be eliminated at least partly.

In addition to the above-mentioned reductants, CO and/or H<sub>2</sub>, optionally supplemented with hydrocarbons, also ammonia (NH<sub>3</sub>) can be formed in the presence of hydrogen and nitrogen, under suitable process

conditions, because of the position of the chemical equilibrium  $3\text{H}_2 + \text{N}_2 = 2\text{NH}_3$ . As mentioned above, ammonia is a good reductant.

The use of a part of the exhaust gases as a source of hydrocarbons and certainly as an oxidation source for the (catalytic) partial oxidation and/or steam reforming has as a major advantage over the existing technology that the emission of uncombusted hydrocarbons can be minimized, the oxygen content in the total exhaust gas stream decreases, so that the conditions for deNO<sub>x</sub>-ing improve and the energy present in the form of heat in the exhaust gases can be used directly for the catalytic process without making use of extra heat exchanging surface.

Another advantage is that no pure H<sub>2</sub> or H<sub>2</sub> with small amounts of carbon monoxide needs to be produced. As a consequence, it is possible to omit shift reactors and membrane technology.

The reductant forming step can be a partial oxidation step, in which use can be made of a partial oxidation catalyst. In addition, it is possible to carry out the partial oxidation without catalyst, for instance by supplying a controlled amount of energy to a fuel stream, for instance by means of an electrical discharge. Also, the reductant forming step can be a steam reforming step in which use is made of a steam reforming catalyst. A combination of partial oxidation and steam reforming is also possible.

A suitable reductant forming catalyst is, for instance, a partial oxidation catalyst. In the presence of such a catalyst, the partial oxidation of hydrocarbons takes place. As mentioned, according to the invention, the oxygen needed for this partial oxidation is derived from the effluent of the combustion unit, optionally supplemented with oxygen obtained from elsewhere, coming, for instance, from added air. The product stream of the partial oxidation step is highly suitable for use as reductant stream.

Another possibility of preparing a stream comprising H<sub>2</sub> and/or CO, and optionally hydrocarbons, from a stream comprising hydrocarbons, is the use of a so-called steam reforming. In steam reforming, in addition to hydrocarbons, water is to be added to the steam reforming step. This water may originate from the effluent of the combustion engine, from a separate stock, or from a combination of these two sources. In steam reforming, hydrocarbons are converted with water (steam) to a mixture of hydrocarbons, such as methane, and/or H<sub>2</sub> and CO<sub>2</sub>. As a consequence of

chemical equilibria, in addition to these components, CO may also be present. The mixture thus formed is very suitable to be used as a reductant stream.

5 Next, the reductant stream, together with the effluent of the combustion unit, is contacted with a deNO<sub>x</sub> catalyst so that the desired conversion of nitrogen oxides takes place.

The in situ production of the reductant offers a number of important advantages. Thus, according to the invention, the supply of reductants can take place continuously, in the case of natural gas, or in any 10 case simultaneously with the supply of the fuel for the combustion unit, and it is no longer necessary to have and maintain a separate stock thereof. This can be practical, for instance, when used in mobile combustion units, such as trucks or passenger cars, because then no separate storage tanks for the reducing agent need to be present. This may also be an important 15 advantage in stationary units. The fact that no ammonia and urea (whether or not as a urea solution) are used, at least do not need to be drawn from elsewhere, is also an advantage because the above-outlined disadvantages associated with the use of these reductants no longer occur.

Another advantage of the invention arises if hydrocarbons from the 20 effluent of the combustion unit are used as feedstock for the reductant forming step, as a result of which the amounts of hydrocarbons in the exhaust gas will then be lowered in that they are used for the reaction with NO<sub>x</sub>. Such a reduction is favorable, since the emission of hydrocarbons is undesirable from an environmental point of view. Another advantage of the 25 use of the effluent of the combustion unit for the formation of the reducing gas is the decrease of the amount of hydrocarbons needed for the reductant formation.

Accordingly, the present invention is characterized by a method for 30 reducing the content of nitrogen oxides in a nitrogen oxide- and oxygen-containing gas stream by contacting this gas stream in the presence of a deNO<sub>x</sub> catalyst with a reducing gas stream, which comprises CO, H<sub>2</sub> and possibly NH<sub>3</sub> and which reducing gas stream has been obtained by 35 converting hydrocarbons with the oxygen from the nitrogen oxide- and oxygen-containing gas stream, optionally in the presence of a reductant forming catalyst.

According to a preferred embodiment, the nitrogen oxide- and oxygen-containing gas stream is the effluent of a step for combusting fuels, which comprises the steps of feeding at least a stream a) comprising one or more fuels and a stream b) containing excess oxygen with respect to the fuel, which further comprises nitrogen, wherein the effluent, together with the reducing gas stream c) which further optionally comprises one or more hydrocarbons, is contacted with the deNO<sub>x</sub> catalyst, wherein to stream c) no ammonia and no urea is added and wherein stream c) has been substantially obtained by contacting streams d) and e) with the reductant forming catalyst, stream d) comprising one or more hydrocarbons and stream e) comprising oxygen and water.

The combustion unit is suitable for generating heat, and optionally energy. The combustion unit can work on the basis of a flame, but the combustion in the combustion unit can also proceed by catalytic route. Preferably, the combustion unit is a gas engine, gas turbine, diesel engine or gasoline engine.

A stream c) which is substantially free from externally added ammonia and urea is understood to mean that to this stream, in accordance with the invention, no reductants of this type need to be added. Still, ammonia and possibly compounds derived therefrom, such as urea, can be present as a result of the above-mentioned equilibrium reaction of N<sub>2</sub> and H<sub>2</sub>.

According to the present invention, the NO<sub>x</sub> is reduced with a mixture of H<sub>2</sub>, CO and possibly NH<sub>3</sub>. In addition, hydrocarbons which have not been (entirely) converted can be present in the reducing gas stream. These hydrocarbons also work as reductants. The reducing gas mixture is obtained by converting the hydrocarbons from a part of the exhaust gas stream with optionally extra added hydrocarbons, by means of (catalytic) partial oxidation, steam reforming or a combination of both technologies by means of the oxygen and water vapor present in the same part of the exhaust gas stream and optionally externally added air and/or water vapor. Optionally, extra reducing agent such as hydrogen can be added to the reducing gas mixture obtained.

Particularly preferred is the method and the apparatus suitable therefor according to the invention, wherein the engine comprises a heat

exchanger, such that at least a portion of the heat released upon the combustion can be usefully employed, for instance for heating, as of greenhouses or other spaces. Such units, in which at the same time both heat and energy are generated, the energy being typically in the form of 5 electrical power, are also referred to as combined heat and power units or total energy plants.

The invention can also be applied in various means of transport such as vessels, airplanes, trucks and passenger cars and trains provided with a hydrocarbon-fired locomotive engine.

10 The method according to the invention and the apparatuses suitable therefor is suitable in particular for operating combustion units under so-called lean-burn conditions, i.e., conditions where the ratio between the streams a) and b) is selected such that the amount of oxygen is at least the amount needed for the complete combustion of the fuels in 15 stream a). These are the conditions under which oxygen is present in the effluent of the combustion unit and wherein, with advantage, the deNO<sub>x</sub> reaction with the effluent of the catalytic partial oxidation step can be carried out.

20 Suitable fuels for the feedstock a) are hydrocarbons and/or synthesis gas (CO/H<sub>2</sub> mixture).

Preferably, the hydrocarbons for the reductant forming step are at least partly drawn from the same source as the fuel for the combustion unit. In this case, stream a) and stream d) comprise the same components.

25 In order to reduce the content of hydrocarbons in the emission of the apparatus for the method according to the invention, the hydrocarbons that are present in the effluent of the combustion unit are at least partly used as feedstock for the reductant forming step, which may or may not be supplemented with a hydrocarbon stream drawn from elsewhere.

30 In order to keep the oxygen content low when contacting the streams with the deNO<sub>x</sub> catalyst, the effluent of the combustion unit is used as oxygen source, which may or may not be supplemented with an oxygen stream drawn from elsewhere.

35 As fuel for the combustion unit and/or as feedstock for the reductant forming step, besides synthesis gas, in principle all hydrocarbons suitable therefor can be used. It is practically preferred, however, when the

hydrocarbons from stream a) and d) are selected independently from the group consisting of natural gas (which comprises substantially methane), methane, diesel oil, gasoline, fuel oil, methanol, ethanol, naphtha, kerosene, ethane, propane, butane, LPG, derivatives and mixtures thereof.

5. The catalyst for converting nitrogen oxides can be selected from the group of catalysts which catalyze the reduction of NO<sub>x</sub>, such as the conventional catalysts for removal of NO<sub>x</sub>. Preferably, these are selected from the group comprising zeolites, metal-exchanged zeolites, such as Co-, Cu- and/or Ce-exchanged zeolites, Pt, Rh and/or Ir catalyst, optionally provided on a support such as a washcoat which may further comprise Ba, 10 La, Y, Sr, Pr, Ce, Si, Ti, Al and/or Zr.

15. The catalyst for the partial oxidation of hydrocarbons can be selected from the group consisting of Pt, Rh, Ru, Pd, Co and Ni, if desired provided on suitable supports such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, silica/alumina-zeolites and mixtures thereof, optionally stabilized with, for instance, Si, La, Ba or Y and mixtures thereof.

20. The steam reforming catalyst which is capable of converting a mixture of hydrocarbons and water to a mixture of H<sub>2</sub>, CO, CO<sub>2</sub> and/or hydrocarbons can be any conventional steam reforming catalyst, which may or may not be supported, according to conventional techniques, as known to the skilled person. Preferably, the steam reforming catalyst is a supported catalyst comprising Ni, Rh and/or Pt.

25. For operating an apparatus according to the invention, factors such as hydrocarbon/oxygen ratio, temperature, pressure, residence time and/or amount of catalyst for the partial oxidation of hydrocarbons should be selected such that no complete oxidation takes place. The molar hydrocarbon/oxygen ratio is expressed in  $\lambda_{PO}$ , such that for stoichiometric ratios (i.e., precisely sufficient oxygen to effect the complete combustion of the fuel),  $\lambda_{PO} = 1$ . According to the invention,  $\lambda_{PO} < 1$ . Preferably,  $0.2 < \lambda_{PO} < 30$  0.7.  $\lambda_{PO}$  is controllable by adjusting the air/fuel amount and is dependent on the hydrocarbons used.

35. The temperature for the reductant forming step is generally between 250 and 1100°C. The residence time for the reductant forming step is generally between 200 en 150,000 h<sup>-1</sup>. Although the pressure will also have an influence, it is generally dictated by the other process conditions. In

general, the pressure will be atmospheric or slightly higher and not higher than 50 bars.

The use of an SCR catalyst as a method of converting NO<sub>x</sub> with a reducing agent to N<sub>2</sub> often has the limitation that sufficient conversion of NO<sub>x</sub> can be achieved in a limited temperature frame. Thus, in DE-A-5 196 00 558, as a practical example, a conversion curve of NO<sub>x</sub> as a function of the temperature is given, in which a conversion of 40% is achieved. This is typical of SCR systems that do not work with NH<sub>3</sub> or urea as reducing agent. Selecting the process conditions of the reductant forming step such 10 that also NH<sub>3</sub> is generated is therefore advantageous because then a higher NO<sub>x</sub> conversion can be achieved.

When a high conversion of NO<sub>x</sub> is required, as, for instance, in the application of exhaust gases as fertilizing gas in horticulture, it is better for the method according to the present invention to be carried out with an NO<sub>x</sub> 15 storage system, instead of an SCR system. If the deNO<sub>x</sub> step is carried out with such an NO<sub>x</sub> storage system (also referred to as NO<sub>x</sub> Storage and Reduction Catalyst, NSR), such as described, for instance, in N. Takhashi et al., Environmental Catalysis, p. 45, (1995), a very high conversion in NO<sub>x</sub> can be obtained. According to this method, nitrogen oxides are 20 absorbed from the nitrogen oxide- and oxygen-containing gas stream to a suitable absorbent and subsequently, for instance by switching, the reducing gas stream is contacted with the absorbent. The deNO<sub>x</sub> step is thus operated discontinuously. A very effective NO<sub>x</sub> removal can thus be obtained.

With this NO<sub>x</sub> storage system, it is possible to absorb NO<sub>x</sub> in an 25 oxidizing medium ( $\lambda < 1$ ), and in a reducing medium ( $\lambda < 1$ ) to convert both the NO<sub>x</sub> in the exhaust gas and the adsorbed NO<sub>x</sub> to nitrogen. The catalyst in the NO<sub>x</sub> storage system can very suitably consist of platinum provided on a barium-containing and/or zeolite-comprising alumina washcoat. The 30 barium present can react with NO<sub>x</sub> to barium nitrate. This nitrate salt decomposes in a reducing medium to barium and N<sub>2</sub>.

The NO<sub>x</sub> storage system can be operated according to the invention by passing the exhaust gases through the NO<sub>x</sub> storage system until the system is saturated with NO<sub>x</sub>. Thereafter, regeneration can be done with a 35 reducing agent which has been obtained as described above. Optionally, this

reducing agent can be supplemented with a reduction agent drawn from elsewhere.

Preferably, this NOx storage system is designed with minimally two parallel beds. One bed is used to absorb NOx, while the other bed is 5 regenerated. As soon as the former bed is saturated and/or the second bed is sufficiently regenerated, the streams are switched, so that the regenerated bed can proceed to absorb NOx and the loaded NOx bed is regenerated in that the absorbed NOx is converted to nitrogen.

The effluent of the regeneration step of the NOx storage bed can be 10 recirculated with advantage and, together with the inlet air, be passed to the inlet of the combustion unit (for instance a gas engine). This provides at least two advantages. In the first place, in this way no CO-containing gas needs to be discharged. In the second place, according to this embodiment, it is of less importance to obtain a complete conversion of hydrocarbons to 15 CO/H<sub>2</sub> in the preceding preparation step of the reducing gas stream.

Both the deNOx catalyst and the reductant forming catalyst can be present in the method according to the invention in the forms known to those skilled in the art, as in the form of a bed of granules, extrusions, 20 granules, and/or pellets, or provided on ceramic or so-called metal monoliths, or differently structured forms.

The use of the catalyst in structured form is preferred because this allows other relevant factors for the method, such as pressure drop, mixing, contact time, heat management, mechanical strength and life, to be tailored to the prevailing conditions through suitable choices, and the method can 25 thereby be optimized.

The invention is therefore characterized by the use of a catalyst suitable for converting nitrogen oxides in combination with either a catalyst suitable for the partial oxidation of hydrocarbons, or a catalyst suitable for steam reforming, for converting nitrogen oxides in generating heat and 30 optionally energy from hydrocarbons, without this requiring ammonia or urea to be added externally.

## CLAIMS

1. A method for reducing the content of nitrogen oxides in a nitrogen oxide- and oxygen-containing gas stream by contacting this gas stream in the presence of a deNOx catalyst with a reducing gas stream, which comprises CO, H<sub>2</sub> and possibly NH<sub>3</sub> and which reducing gas stream has been obtained by converting hydrocarbons with oxygen and/or water from said nitrogen oxide- and oxygen-containing gas stream, if desired in the presence of a reductant forming catalyst.  
5
2. A method according to claim 1, wherein substantially all of the oxygen present in the part of said nitrogen oxide- and oxygen-containing gas stream that is used for the reductant formation is used up.  
10
3. A method according to any one of the preceding claims, wherein said nitrogen oxide- and oxygen-containing gas stream is the effluent of a step for combusting fuels, which comprises the steps of feeding at least a stream a) comprising one or more fuels and a stream b) containing excess oxygen with respect to the fuel; wherein said effluent, together with said reducing gas stream c) which further optionally comprises one or more hydrocarbons, is contacted with said deNOx catalyst; wherein to stream c) no ammonia and no urea is added; and wherein stream c) has been substantially obtained by subjecting streams d) and e) to a reductant forming step, while stream d) comprises one or more hydrocarbons.  
15  
20
4. A method according to any one of the preceding claims, wherein said nitrogen oxide- and oxygen-containing gas stream originates from a combined heat and power unit.
5. A method according to any one of the preceding claims, wherein said reducing gas stream is obtained by carrying out a partial oxidation step, utilizing a partial oxidation catalyst, or a steam reforming step, utilizing a steam reforming catalyst.  
25
6. A method according to any one of claims 3-5, wherein the fuel in stream a) comprises synthesis gas and/or one or more hydrocarbons.

7. A method according to any one of claims 3-6, wherein stream a) and stream d) comprise at least partly the same compounds.

8. A method according to any one of claims 3-7, wherein the fuel in stream a) comprises hydrocarbons which, like the hydrocarbons in stream d), have been selected independently from the group consisting of natural gas, methane, diesel oil, gasoline, fuel oil, methanol, ethanol, naphtha, kerosene, ethane, propane, butane, LPG, and mixtures thereof.

9. A method according to any one of the preceding claims, wherein a reductant forming catalyst is used which is a partial oxidation catalyst for the partial oxidation of hydrocarbons, selected from the group consisting of Pt, Rh, Ru, Pd, Co and Ni and combinations thereof, optionally provided on a support, which support is optionally stabilized with Si, La, Ba and/or Y.

10. A method according to any one of the preceding claims, wherein the reductant forming catalyst is a steam reforming catalyst which comprises Ni, Rh and/or Pt.

11. A method according to any one of the preceding claims, wherein the reductant forming step is a partial oxidation step, wherein the ratio of hydrocarbons and oxygen is selected such that no complete oxidation takes place.

12. A method according to any one of the preceding claims, wherein nitrogen oxides from the nitrogen oxide- and oxygen-containing gas stream are absorbed onto a suitable absorbent and subsequently said reducing gas stream is contacted with said absorbent.

13. A method according to claim 12, wherein said absorbent is a barium and/or zeolite comprising alumina washcoat on a structured support.

14. A method according to claim 12 or 13, wherein the product that is formed in the step wherein stream c) is contacted with the structured support is used as fuel for a gas engine.

# INTERNATIONAL SEARCH REPORT

Inte. onal Application No

PCT/NL 00/00404

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 7 B01D53/94 B01D53/86

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
 IPC 7 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 197 42 705 A (MAZDA MOTOR CORP.) 2 April 1998 (1998-04-02)	1-11
Y	column 3, line 54 -column 4, line 63 ---	12,13
X	EP 0 441 401 A (TOYOTA JIDOSHA KABUSHIKI KAISHA) 14 August 1991 (1991-08-14) column 3, line 28 -column 5, line 27 ---	1-9,11
X	DE 196 36 790 A (VOLKSWAGEN AG) 12 March 1998 (1998-03-12) column 8, line 26 -column 9, line 37 ---	1-13
X	WO 98 09699 A (THE REGENTS OF THE UNIVERSITY OF CALIFORNIA) 12 March 1998 (1998-03-12) page 13, line 15 -page 118, line 13 ---	1-4,6-8, 11 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

26 September 2000

Date of mailing of the international search report

04/10/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040; Tx. 31 651 epo nl,  
Fax (+31-70) 340-3016

Authorized officer

Doolan, G

# INTERNATIONAL SEARCH REPORT

Inte	ional Application No
PCT/NL 00/00404	

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Description of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE 195 43 219 C (MERCEDES-BENZ AKTIENGESELLSCHAFT) 5 December 1996 (1996-12-05) column 2, line 43 -column 4, line 4 ----	12,13
A	EP 0 537 968 A (TOYOTA JIDOSHA KABUSHIKI KAISHA) 21 April 1993 (1993-04-21) column 4, line 32 -column 9, line 18 ----	1-11
A	DE 42 30 408 A (AISIN SEIKI K. K.) 18 March 1993 (1993-03-18) column 4, line 50 -column 6, line 8 column 7, line 65 -column 8, line 34 ----	1-8,10
A	DE 44 04 617 A (DAIMLER-BENZ AKTIENGESELLSCHAFT) 17 August 1995 (1995-08-17) column 1, line 37 -column 2, line 30 ----	1-9,11
A	DE 196 00 558 A (DAIMLER-BENZ AKTIENGESELLSCHAFT) 10 July 1997 (1997-07-10) column 2, line 32 -column 4, line 45 ----	1-11

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int'l	Application No
PCT/NL 00/00404	

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
DE 19742705 A	02-04-1998	JP 10151353 A US 6066587 A		09-06-1998 23-05-2000
EP 441401 A	14-08-1991	JP 2850547 B JP 4214918 A DE 69109315 D DE 69109315 T US 5189876 A		27-01-1999 05-08-1992 08-06-1995 12-10-1995 02-03-1993
DE 19636790 A	12-03-1998	EP 0829623 A		18-03-1998
WO 9809699 A	12-03-1998	US 5711147 A US 5891409 A EP 0946256 A US 6038853 A US 6038854 A US 5893267 A		27-01-1998 06-04-1999 06-10-1999 21-03-2000 21-03-2000 13-04-1999
DE 19543219 C	05-12-1996	FR 2741385 A GB 2307311 A, B IT RM960768 A US 5771686 A		23-05-1997 21-05-1997 08-05-1998 30-06-1998
EP 537968 A	21-04-1993	JP 5106430 A DE 69207854 D DE 69207854 T US 5412946 A		27-04-1993 07-03-1996 05-06-1996 09-05-1995
DE 4230408 A	18-03-1993	JP 5071334 A NL 9201586 A US 5441401 A		23-03-1993 01-04-1993 15-08-1995
DE 4404617 A	17-08-1995	US 5586433 A		24-12-1996
DE 19600558 A	10-07-1997	EP 0783918 A US 5921076 A		16-07-1997 13-07-1999